### **New Directions in Catalysis: Nanostructured Membranes**

#### **Scientific Achievement**

Atomic layer deposition (ALD) was used to precisely control the chemical deposition on the walls of the anodized aluminum oxide (AAO) pores to produce nanoporous membranes that have shown promising catalytic properties. ALD is a growth technique that uses alternating, saturating reactions between gaseous precursor molecules and a substrate to deposit films in a layer-by-layer fashion. By repeating the binary reaction sequence in an ABAB... fashion, films of micrometer thickness can be deposited with atomic layer precision. With careful optimization of experimental conditions, we have been able to produce high quality AAO membranes coated by ALD in a layer by layer manner for a wide variety of materials (Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZnO, and V<sub>2</sub>O<sub>5</sub>) with pore diameters narrowed from 38 nm to 5 nm. The new inorganic catalytic membranes synthesized in this program, using a combination of AAO and gas phase ALD, have been tested for catalytic activity. They were found to exhibit a surprising specificity and a high conversion rate for oxidative dehydrogenation of cyclohexane to cyclohexene. (M. J. Pellin, P. C. Stair, G. Xiong, J. W. Elam, J. Birrell, L. Curtiss, S. M. George, C. Y. Han, L. Iton, H. Kung, M. Kung, H. H. Wang, Catalysis Letters, 102 127 (2005).) These results demonstrate a new approach for tuning the surface reactivity of membranes through atomic level control of both pore wall diameter and composition. The wide range of molecular precursors that can be used in the reaction sequence allows for precise control of the chemical reactivity.

### Significance

This opens up numerous opportunities for development of new catalytic membranes. We enter an era where the synthesis of materials can be controlled in a nearly atom-by-atom fashion, which will tremendously advance the frontiers of catalysis. In order to use this capability a fundamental scientific understanding of the relationship between the composition/structure of the catalyst/substrate and the catalytic reaction mechanism must be developed. The new nanoporous material based on AAO and ALD exploits unprecedented atomic level control of for catalysis. The nanoporous membranes can be used as supports for encapsulated catalytic clusters, complexes, or nanoparticles to systematically investigate their properties and achieve a fundamental understanding of controlling parameters for these materials.

The research on tailoring the catalytic membranes represents a fundamental research effort that has gone across divisional programs and divisions. It includes synthesis, characterization, catalyst testing, and theory components. The core Materials Science program has been the driver for the materials development work, which has led to a new BES-Chemical Science program for studies of fundamental catalytic processes and an EERE-Office of Industrial Technology program on development of highly selective oxidation catalysts.

### **Performers:**

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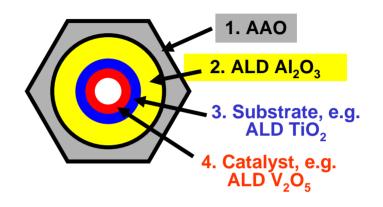
P. Stair (NWU, CHM), J. Elam (ES), H. Feng (CHM), P. Redfern (CHM), S. Zygmunt (Valparaiso) and H. Kung (NWU)

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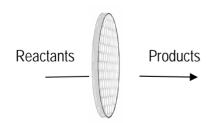
This is a <u>multi-program effort</u> that is using an unique nanoporous membrane architecture developed in the Materials Science Program to advance molecular-level understanding and control of pathways for selective catalytic oxidation.

Four synergistic components: synthesis, characterization, catalytic activity, and theory

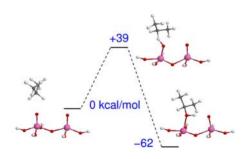
## Synthesis of Nanoporous Membrane Catalyst



# Improved conversion and selectivity for catalytic oxidation



# Simulation And Modeling: Materials and Reaction



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